To optimize graphite furnace conditions, carefully adjust furnace temperature settings to maximize sensitivity and precision and to minimize interferences. Follow manufacturer's instructions.

Use drying temperatures slightly above the solvent boiling point to provide enough time and temperature for complete evaporation without boiling or spattering.

The charring temperature must be high enough to maximize volatilization of interfering matrix components yet too low to volatilize the element of interest. With the drying and atomization temperatures set to their optimum values, analyze a standard at a series of charring temperatures in increasing increments of 50 to 100°C. When the optimum charring temperature is exceeded, there will be a significant drop in sensitivity. Plot charring temperature versus sample absorbance: the optimum charring temperature is the highest temperature without reduced sensitivity.

Select atomization temperature by determining the temperature providing maximum sensitivity without significantly eroding precision. Optimize by a series of successive determinations at various atomization temperatures using a standard solution giving an absorbance of 0.2 to 0.5.

c. Instrument calibration: Prepare standards for instrument calibration by dilution of the metal stock solutions. Prepare standards fresh daily.

Prepare a blank and at least three calibration standards in the appropriate concentration range (See Table 3113:II) for correlating element concentration and instrument response. Match the matrix of the standard solutions to those of the samples as closely as possible. In most cases, this simply requires matching the acid background of the samples. For seawaters or brines, however, use the metal-free matrix (¶ 3*g*) as the standard solution diluent. In addition, add the same concentration of matrix modifier (if required for sample analysis) to the standard solutions.

Inject a suitable portion of each standard solution, in order of increasing concentration. Analyze each standard solution in triplicate to verify method precision.

Construct an analytical curve by plotting the average peak absorbencies or peak areas of the standard solution versus concentration on linear graph paper. Alternatively, use electronic instrument calibration if the instrument has this capability.

d. Sample analysis: Analyze all samples except those demonstrated to be free of matrix interferences (based on recoveries of 85%–115% for known additions) using the method of standard additions. Analyze all samples at least in duplicate or until reproducible results are obtained. A variation of ≤ 10% is considered acceptable reproducibility. Average replicate values.

1) Direct determination—Inject a measured portion of pretreated sample into the graphite furnace. Use the same volume as was used to prepare the calibration curve. Dry, char, and atomize according to the preset program. Repeat until reproducible results are obtained.

Compare the average absorbance value or peak area to the calibration curve to determine concentration of the element of interest. Alternatively, read results directly if the instrument is equipped with this capability. If absorbance (or concentration) or peak area of the most concentrated sample is greater than absorbance (concentration) or peak area of the standard, dilute sample and reanalyze. If very large dilutions are required, another technique (e.g., flame AA or ICP) may be more suitable for this sample. Large dilution factors magnify small errors on final calculation. Keep acid background and concentration of matrix modifier (if required) constant. If sample is diluted with water, add acid and matrix modifier to restore the concentration of both to the original. Alternatively, dilute the sample in a blank solution of acid and matrix modifiers.

Proceed to ¶ 5*a* below.

2) Method of standard additions—Refer to ¶ 4*c* above. The method of standard additions is valid only when it falls in the linear portion of the calibration curve. Once instrument sensitivity has been optimized for the element of interest and the linear range for the element has been established, proceed with sample analyses.

Inject a measured volume of sample into furnace device. Dry, char or ash, and atomize samples according to preset program. Repeat until reproducible results are obtained. Record instrument response in absorbance or concentration as appropriate. Add a known concentration of the element of interest to a separate portion of sample so as not to change significantly the sample volume. Repeat the determination.

Add a known concentration (preferably twice that used in the first addition) to a separate sample portion. Mix well and repeat the determination.

Plot average absorbance or instrument response for the sample and the two portions with known additions on the vertical axis with the concentrations of element added on the horizontal axis of linear graph paper. Draw a straight line connecting the three points and extrapolate to zero absorbance. The intercept at the horizontal axis is the concentration of the sample. The concentration axis to the left of the origin should be a mirror image of the axis to the right.

5. Calculations

a. Direct determination:

$$\mu g \text{ metal/L} = C \times F$$

where:

C = metal concentration as read directly from the instrument or from the calibration curve, μg/L, and
F = dilution factor.

b. Method of additions:

$$\mu g \text{ metal/L} = C \times F$$

where:

C = metal concentration as read from the method of additions plot, μg/L, and
F = dilution factor.

6. Precision and Bias

Data typical of the precision and bias obtainable are presented in Tables 3113:III, IV, and V.

7. Quality Control

See Section 3020 for specific quality control procedures to be followed during analysis. Although previous indications were

TABLE 3113:III. INTERLABORATORY SINGLE-ANALYST PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

Element	Concentration µg/L	Single-Analyst Precision % RSD: Lab Pure	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28	66	108	70	—	—	66
	125	27	35	24	—	—	34
	11 000	11	—	—	22	—	—
	58 300	27	—	—	19	—	—
	460	9	—	—	—	30	—
	2 180	28	—	—	—	4	—
As	10.5	20	13	13	13	56	18
	230	10	18	13	21	94	14
	9.78	40	25	15	74	23	11
Ba	227	10	6	8	11	15	6
	56.5	36	21	29	59	23	27
Be	418	14	12	20	24	24	18
	0.45	18	27	15	30	2	11
Cd	10.9	14	4	9	7	12	12
	0.43	72	49	1	121	35	27
Cr	12	11	17	22	14	11	15
	9.87	24	33	10	23	15	10
Co	236	16	7	11	13	16	7
	29.7	10	17	10	19	24	12
Cu	420	8	11	13	14	9	5
	10.1	49	47	17	17	—	30
Fe	234	8	15	6	21	—	11
	300	6	—	—	—	11	—
	1 670	11	—	—	—	6	—
Pb	26.1	144	52	153	—	—	124
	455	48	37	45	—	—	31
	1 030	17	—	—	30	—	—
	5 590	6	—	—	32	—	—
	370	14	—	—	—	19	—
	2 610	9	—	—	—	18	—
Mn	10.4	6	19	17	21	19	33
	243	17	7	17	18	12	16
Ni	0.44	187	180	—	—	—	275
	14.8	32	19	—	—	—	18
	91.0	15	—	—	48	—	—
	484.0	4	—	—	12	—	—
	111.0	12	—	—	—	21	—
	666.0	6	—	—	—	20	—
Se	26.2	20	26	25	24	18	9
	461.0	15	11	9	8	11	4
Ag	10.0	12	27	16	35	41	13
	235.0	6	6	15	6	13	14
	8.48	10	—	—	15	27	16
	56.5	14	—	—	7	16	23
	0.45	27	166	48	—	—	—
	13.6	15	4	10	—	—	—

that very low optimum concentration ranges were attainable for most metals (see Table 3113:II). data in Table 3113:III using variations of these protocols show that this may not be so. Exercise extreme caution when applying this method to the lower concentration ranges. Verify analyst precision at the beginning of each analytical run by making triplicate analyses.

8. Reference

1. COPELAND, T.R. & J.P. MANEY. 1986. EPA Method Study 31: Trace Metals by Atomic Absorption (Furnace Techniques). EPA-600/S4-85-070. U.S. Environmental Protection Agency. Environmental Monitoring and Support Lab., Cincinnati, Ohio.

TABLE 3113:IV. INTERLABORATORY OVERALL PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

Element	Concentration µg/L	Overall Precision % RSD: Lab Pure	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28	99	114	124	—	—	131
	125	45	47	49	—	—	40
	11 000	19	—	—	43	—	—
	58 300	31	—	—	32	—	—
	460	20	—	—	—	47	—
	2 180	30	—	—	—	15	—
	10.5	37	19	22	50	103	39
	230	26	16	16	17	180	21
As	9.78	43	26	37	72	50	39
	227	18	12	13	20	15	14
Ba	56.5	68	38	43	116	43	65
	418	35	35	28	38	48	16
Be	0.45	28	31	15	67	50	35
	10.9	33	15	26	20	9	19
Cd	0.43	73	60	5	88	43	65
	12	19	25	41	26	20	27
Cr	9.87	30	53	24	60	41	23
	236	18	14	24	20	14	20
Co	29.7	13	26	17	18	21	17
	420	21	21	17	18	13	13
Cu	10.1	58	82	31	32	—	74
	234	12	33	19	21	—	26
	300	13	—	—	—	14	—
	1 670	12	—	—	—	13	—
Fe	26.1	115	93	306	—	—	204
	455	53	46	53	—	—	44
	1 030	32	—	—	25	—	—
	5 590	10	—	—	43	—	—
	370	28	—	—	—	22	—
	2 610	13	—	—	—	22	—
Pb	10.4	27	42	31	23	28	47
	243	18	19	17	19	19	25
Mn	0.44	299	272	—	—	—	248
	14.8	52	41	—	—	—	29
	91.0	16	—	—	45	—	—
	484.0	5	—	—	17	—	—
	111.0	15	—	—	—	17	—
	666.0	8	—	—	—	24	—
Ni	26.2	35	30	49	35	37	43
	461.0	23	22	15	12	21	17
Se	10.0	17	48	32	30	44	51
	235.0	16	18	18	17	22	34
Ag	8.48	23	—	—	16	35	34
	56.5	15	—	—	24	32	28
	0.45	57	90	368	—	—	—
	13.6	19	19	59	—	—	—

TABLE 3113:V. INTERLABORATORY RELATIVE ERROR DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

Element	Concentration µg/L	Relative Error %					
		Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28.0	86	150	54	—	—	126
	125.0	4	41	39	—	—	30
	11 000.0	2	—	—	14	—	—
	58 300.0	12	—	—	7	—	—
	460.0	2	—	—	—	11	—
	2 180.0	11	—	—	—	9	—
Sb	10.5	30	32	28	24	28	36
	230.0	35	14	19	13	73	39
As	9.78	36	1	22	106	13	16
	227.0	3	7	10	19	6	13
Ba	56.5	132	54	44	116	59	40
	418.0	4	0	0	13	6	60
Be	0.45	40	16	11	16	10	15
	10.9	13	2	9	7	8	8
Cd	0.43	58	45	37	66	16	19
	12.0	4	6	5	22	18	3
Cr	9.87	10	9	4	2	5	15
	236.0	11	0	9	13	5	8
Co	29.7	7	7	1	6	3	13
	420.0	12	8	8	11	5	18
Cu	10.1	16	48	2	5	—	15
	234.0	8	7	0	4	—	19
	300.0	4	—	—	—	21	—
	1 670.0	6	—	—	—	2	—
Fe	26.1	85	60	379	—	—	158
	455.0	43	22	31	—	—	18
	1 030.0	8	—	—	8	—	—
	5 590.0	2	—	—	12	—	—
	370.0	4	—	—	—	11	—
	2 610.0	35	—	—	—	2	—
Pb	10.4	16	10	17	1	34	14
	234.0	5	15	8	18	15	29
Mn	0.44	332	304	—	—	—	556
	14.8	10	1	—	—	—	36
	91.0	31	—	—	10	—	—
	484.0	42	—	—	4	—	—
	111.0	1	—	—	—	29	—
	666.0	6	—	—	—	23	—
Ni	26.2	9	16	10	7	33	54
	461.0	15	19	18	31	16	18
Se	10.0	12	9	6	36	17	37
	235.0	7	7	0	13	10	17
Ag	8.48	12	—	—	1	51	20
	56.5	16	—	—	8	51	22
	0.45	34	162	534	—	—	—
	13.6	3	12	5	—	—	—

9. Bibliography

RENSHAW, G.D. 1973. The determination of barium by flameless atomic absorption spectrophotometry using a modified graphite tube atomizer. *Atomic Absorption Newsletter* 12:158.

YANAGISAWA, M., T. TAKEUCHI & M. SUZUKI. 1973. Flameless atomic absorption spectrometry of antimony. *Anal. Chim. Acta* 64:381.

RATTONETTI, A. 1974. Determination of soluble cadmium, lead, silver and indium in rainwater and stream water with the use of flameless atomic absorption. *Anal. Chem.* 46:739.

HENN, E.L. 1975. Determination of selenium in water and industrial effluents by flameless atomic absorption. *Anal. Chem.* 47:428.

MARTIN, T.D. & J.F. KOPP. 1975. Determining selenium in water, wastewater, sediment and sludge by flameless atomic absorption spectrometry. *Atomic Absorption Newsletter* 14:109.

MARUTA, T., K. MINEGISHI & G. SUDOH. 1976. The flameless atomic absorption spectrometric determination of aluminum with a carbon atomization system. *Anal. Chim. Acta* 81:313.

CRANSTON, R.E. & J.W. MURRAY. 1978. The determination of chromium species in natural waters. *Anal. Chim. Acta* 99:275.

HOFFMEISTER, W. 1978. Determination of iron in ultrapure water by atomic absorption spectroscopy. *Z. Anal. Chem.* 50:289.

LAGAS, P. 1978. Determination of beryllium, barium, vanadium and some other elements in water by atomic absorption spectrometry with electrothermal atomization. *Anal. Chim. Acta* 98:261.

CARRONDO, M.J.T., J.N. LESTER & R. PERRY. 1979. Electrothermal atomic absorption determination of total aluminum in waters and waste waters. *Anal. Chim. Acta* 111:291.

NAKAHARA, T. & C.L. CHAKRABARTI. 1979. Direct determination of traces of molybdenum in synthetic sea water by atomic absorption spectrometry with electrothermal atomization and selective volatilization of the salt matrix. *Anal. Chim. Acta* 104:99.

TIMINAGA, M. & Y. UMEZAKI. 1979. Determination of submicrogram amounts of tin by atomic absorption spectrometry with electrothermal atomization. *Anal. Chim. Acta* 110:55.

3114 METALS BY HYDRIDE GENERATION/ATOMIC ABSORPTION SPECTROMETRY*

3114 A. Introduction

For general introductory material on atomic absorption spectrometric methods, see Section 3111A.

Two methods are presented in this section: A manual method and a continuous-flow method especially recommended for selenium. Continuous-flow automated systems are preferable to manual hydride generators because the effect of sudden hydrogen generation on light-path transparency is removed and any blank response from contamination of the HCl reagent by the elements being determined is incorporated into the background base line.

* Approved by Standard Methods Committee, 1989.

3114 B. Manual Hydride Generation/Atomic Absorption Spectrometric Method

1. General Discussion

a. Principle: This method is applicable to the determination of arsenic and selenium by conversion to their hydrides by sodium borohydride reagent and aspiration into an atomic absorption atomizer.

Arsenous acid and selenous acid, the As(III) and Se(IV) oxidation states of arsenic and selenium, respectively, are instantaneously converted by sodium borohydride reagent in acid solution to their volatile hydrides. The hydrides are purged continuously by argon or nitrogen into an appropriate atomizer of an atomic absorption spectrometer and converted to the gas-phase atoms. The sodium borohydride reducing agent, by rapid generation of the elemental hydrides in an appropriate reaction cell, minimizes dilution of the hydrides by the carrier gas and provides rapid, sensitive determinations of arsenic and selenium.

CAUTION: *Arsenic and selenium and their hydrides are toxic. Handle with care.*

At room temperature and solution pH values of 1 or less, arsenic acid, the As(V) oxidation state of arsenic, is reduced relatively slowly by sodium borohydride to As(III), which is then instantaneously converted to arsine. The arsine atomic absorption peaks commonly are decreased by one-fourth to one-third for As(V) when compared to As(III). Determination of total arsenic requires that all inorganic arsenic compounds be in the As(III) state. Organic and inorganic forms of arsenic are first oxidized to As(V) by acid digestion. The As(V) then is quantitatively reduced to As(III) with sodium or potassium iodide before reaction with sodium borohydride.

Selenic acid, the Se(VI) oxidation state of selenium, is not measurably reduced by sodium borohydride. To determine total selenium by atomic absorption and sodium borohydride, first reduce Se(VI) formed during the acid digestion procedure to Se(IV), being careful to prevent reoxidation by chlorine. Efficiency of reduction depends on temperature, reduction time, and HCl concentration. For 4*N* HCl, heat 1 h at 100°C. For 6*N* HCl, boiling for 10 min is sufficient.[1-3] Alternatively, autoclave samples in sealed containers at 121°C for 1 h. NOTE: Autoclaving in sealed containers may result in incomplete reduction, apparently due to the buildup of chlorine gas. To obtain equal instrument

3120 METALS BY PLASMA EMISSION SPECTROSCOPY*

3120 A. Introduction

1. General Discussion

Emission spectroscopy using inductively coupled plasma (ICP) was developed in the mid-1960's[1,2] as a rapid, sensitive, and convenient method for the determination of metals in water and wastewater samples.[3-6] Dissolved metals are determined in filtered and acidified samples. Total metals are determined after appropriate digestion. Care must be taken to ensure that potential interferences are dealt with, especially when dissolved solids exceed 1500 mg/L.

2. References

1. GREENFIELD, S., I.L. JONES & C.T. BERRY. 1964. High-pressure plasma-spectroscopic emission sources. *Analyst* 89: 713.
2. WENDT, R.H. & V.A. FASSEL. 1965. Induction-coupled plasma spectrometric excitation source. *Anal. Chem.* 37:920.
3. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1983. Method 200.7. Inductively coupled plasma-atomic emission spectrometric method for trace element analysis of water and wastes. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020, revised March 1983.
4. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1987. Annual Book of ASTM Standards. Vol. 11.01. American Soc. Testing & Materials, Philadelphia, Pa.
5. FISHMAN, M.J. & W.L. BRADFORD, eds. 1982. A Supplement to Methods for the Determination of Inorganic Substances in Water and Fluvial Sediments. Rep. No. 82-272. U.S. Geological Survey, Washington, D.C.
6. GARBARINO, J.R. & H.E. TAYLOR. 1985. Trace Analysis. Recent Developments and Applications of Inductively Coupled Plasma Emission Spectroscopy to Trace Elemental Analysis of Water. Volume 4. Academic Press, New York, N.Y.

* Approved by Standard Methods Committee, 1989.

3120 B. Inductively Coupled Plasma (ICP) Method

1. General Discussion

a. Principle: An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field typically oscillating at 27.1 MHz. This field is inductively coupled to the ionized gas by a water-cooled coil surrounding a quartz "torch" that supports and confines the plasma. A sample aerosol is generated in an appropriate nebulizer and spray chamber and is carried into the plasma through an injector tube located within the torch. The sample aerosol is injected directly into the ICP, subjecting the constituent atoms to temperatures of about 6000 to 8000°K.[1] Because this results in almost complete dissociation of molecules, significant reduction in chemical interferences is achieved. The high temperature of the plasma excites atomic emission efficiently. Ionization of a high percentage of atoms produces ionic emission spectra. The ICP provides an optically "thin" source that is not subject to self-absorption except at very high concentrations. Thus linear dynamic ranges of four to six orders of magnitude are observed for many elements.[2]

The efficient excitation provided by the ICP results in low detection limits for many elements. This, coupled with the extended dynamic range, permits effective multielement determination of metals.[3] The light emitted from the ICP is focused onto the entrance slit of either a monochromator or a polychromator that effects dispersion. A precisely aligned exit slit is used to isolate a portion of the emission spectrum for intensity measurement using a photomultiplier tube. The monochromator uses a single exit slit/photomultiplier and may use a computer-controlled scanning mechanism to examine emission wavelengths sequentially. The polychromator uses multiple fixed exit slits and corresponding photomultiplier tubes; it simultaneously monitors all configured wavelengths using a computer-controlled readout system. The sequential approach provides greater wavelength selection while the simultaneous approach can provide greater sample throughput.

b. Applicable metals and analytical limits: Table 3120:I lists elements for which this method applies, recommended analytical wavelengths, and typical estimated instrument detection limits using conventional pneumatic nebulization. Actual working detection limits are sample-dependent. Typical upper limits for linear calibration also are included in Table 3120:I.

c. Interferences: Interferences may be categorized as follows:

1) Spectral interferences—Light emission from spectral sources other than the element of interest may contribute to apparent net signal intensity. Sources of spectral interference include direct spectral line overlaps, broadened wings of intense spectral lines, ion-atom recombination continuum emission, molecular band emission, and stray (scattered) light from the emission of elements at high concentrations.[4] Avoid line overlaps by selecting alternate analytical wavelengths. Avoid or minimize other spectral interference by judicious choice of background correction positions. A wavelength scan of the element line region is useful for detecting potential spectral interferences and for selecting positions for background correction. Make corrections for residual spectral interference using empirically determined correction factors in conjunction with the computer software supplied by the spectrometer manufacturer or with the calculation detailed below. The empirical correction method cannot be used with scanning spectrometer systems if the analytical and interfering lines cannot be precisely and reproducibly located. In addition, if using a polychromator, verify absence of spectral interference from an element that could occur in a sample but for which there

TABLE 3120:I. SUGGESTED WAVELENGTHS, ESTIMATED DETECTION LIMITS, ALTERNATE WAVELENGTHS, CALIBRATION CONCENTRATIONS, AND UPPER LIMITS

Element	Suggested Wavelength *nm*	Estimated Detection Limit *µg/L*	Alternate Wavelength* *nm*	Calibration Concentration *mg/L*	Upper Limit Concentration *mg/L*
Aluminum	308.22	40	237.32	10.0	100
Antimony	206.83	30	217.58	10.0	100
Arsenic	193.70	50	189.04†	10.0	100
Barium	455.40	2	493.41	1.0	50
Beryllium	313.04	0.3	234.86	1.0	10
Boron	249.77	5	249.68	1.0	50
Cadmium	226.50	4	214.44	2.0	50
Calcium	317.93	10	315.89	10.0	100
Chromium	267.72	7	206.15	5.0	50
Cobalt	228.62	7	230.79	2.0	50
Copper	324.75	6	219.96	1.0	50
Iron	259.94	7	238.20	10.0	100
Lead	220.35	40	217.00	10.0	100
Lithium	670.78	4‡	—	5.0	100
Magnesium	279.08	30	279.55	10.0	100
Manganese	257.61	2	294.92	2.0	50
Molybdenum	202.03	8	203.84	10.0	100
Nickel	231.60	15	221.65	2.0	50
Potassium	766.49	100‡	769.90	10.0	100
Selenium	196.03	75	203.99	5.0	100
Silica (SiO_2)	212.41	20	251.61	21.4	100
Silver	328.07	7	338.29	2.0	50
Sodium	589.00	30‡	589.59	10.0	100
Strontium	407.77	0.5	421.55	1.0	50
Thallium	190.86†	40	377.57	10.0	100
Vanadium	292.40	8	—	1.0	50
Zinc	213.86	2	206.20	5.0	100

* Other wavelengths may be substituted if they provide the needed sensitivity and are corrected for spectral interference.
† Available with vacuum or inert gas purged optical path.
‡ Sensitive to operating conditions.

is no channel in the detector array. Do this by analyzing single-element solutions of 100 mg/L concentration and noting for each element channel the apparent concentration from the interfering substance that is greater than the element's instrument detection limit.

2) Nonspectral interferences

a) Physical interferences are effects associated with sample nebulization and transport processes. Changes in the physical properties of samples, such as viscosity and surface tension, can cause significant error. This usually occurs when samples containing more than 10% (by volume) acid or more than 1500 mg dissolved solids/L are analyzed using calibration standards containing ≤ 5% acid. Whenever a new or unusual sample matrix is encountered, use the test described in ¶ 4*g*. If physical interference is present, compensate for it by sample dilution, by using matrix-matched calibration standards, or by applying the method of standard addition (see ¶ 5*d* below).

High dissolved solids content also can contribute to instrumental drift by causing salt buildup at the tip of the nebulizer gas orifice. Using prehumidified argon for sample nebulization lessens this problem. Better control of the argon flow rate to the nebulizer using a mass flow controller improves instrument performance.

b) Chemical interferences are caused by molecular compound formation, ionization effects, and thermochemical effects associated with sample vaporization and atomization in the plasma. Normally these effects are not pronounced and can be minimized by careful selection of operating conditions (incident power, plasma observation position, etc.). Chemical interferences are highly dependent on sample matrix and element of interest. As with physical interferences, compensate for them by using matrix matched standards or by standard addition (¶ 5*d*). To determine the presence of chemical interference, follow instructions in ¶ 4*g*.

2. Apparatus

a. ICP source: The ICP source consists of a radio frequency (RF) generator capable of generating at least 1.1 KW of power, torch, tesla coil, load coil, impedance matching network, nebulizer, spray chamber, and drain. High-quality flow regulators are required for both the nebulizer argon and the plasma support gas flow. A peristaltic pump is recommended to regulate sample flow to the nebulizer. The type of nebulizer and spray chamber used may depend on the samples to be analyzed as well as on the equipment manufacturer. In general, pneumatic nebulizers

of the concentric or cross-flow design are used. Viscous samples and samples containing particulates or high dissolved solids content (>5000 mg/L) may require nebulizers of the Babington type.[5]

b. Spectrometer: The spectrometer may be of the simultaneous (polychromator) or sequential (monochromator) type with air-path, inert gas purged, or vacuum optics. A spectral bandpass of 0.05 nm or less is required. The instrument should permit examination of the spectral background surrounding the emission lines used for metals determination. It is necessary to be able to measure and correct for spectral background at one or more positions on either side of the analytical lines.

3. Reagents and Standards

Use reagents that are of ultra-high-purity grade or equivalent. Redistilled acids are acceptable. Except as noted, dry all salts at 105°C for 1 h and store in a desiccator before weighing. Use deionized water prepared by passing water through at least two stages of deionization with mixed bed cation/anion exchange resins.[6] Use deionized water for preparing all calibration standards, reagents, and for dilution.

a. Hydrochloric acid, HCl, conc and 1 + 1.

b. Nitric acid, HNO_3, conc.

c. Nitric acid, HNO_3, 1 + 1: Add 500 mL conc HNO_3 to 400 mL water and dilute to 1 L.

d. Standard stock solutions: See 3111B, 3111D, and 3114B. CAUTION: *Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.*

1) *Aluminum:* See 3111D.3*k*1).
2) *Antimony:* See 3111B.3*j*1).
3) *Arsenic:* See 3114B.3*k*1).
4) *Barium:* See 3111D.3*k*2).
5) *Beryllium:* See 3111D.3*k*3).
6) *Boron: Do not dry* but keep bottle tightly stoppered and store in a desiccator. Dissolve 0.5716 g anhydrous H_3BO_3 in water and dilute to 1000 mL; 1 mL = 100 µg B.
7) *Cadmium:* See 3111B.3*j*3).
8) *Calcium:* See 3111B.3*j*4).
9) *Chromium:* See 3111B.3*j*6).
10) *Cobalt:* See 3111B.3*j*7).
11) *Copper:* See 3111B.3*j*8).
12) *Iron:* See 3111B.3*j*11).
13) *Lead:* See 3111B.3*j*12).
14) *Lithium:* See 3111B.3*j*13).
15) *Magnesium:* See 3111B.3*j*14).
16) *Manganese:* See 3111B.3*j*15).
17) *Molybdenum:* See 3111D.3*k*4).
18) *Nickel:* See 3111B.3*j*16).
19) *Potassium:* See 3111B.3*j*19).
20) *Selenium:* See 3114B.3*n*1).
21) *Silica:* See 3111D.3*k*7).
22) *Silver:* See 3111B.3*j*22).
23) *Sodium:* See 3111B.3*j*23).
24) *Strontium:* See 3111B.3*j*24).
25) *Thallium:* See 3111B.3*j*25).
26) *Vanadium:* See 3111D.3*k*10).
27) *Zinc:* See 3111B.3*j*27).

e. Calibration standards: Prepare mixed calibration standards containing the concentrations shown in Table 3120:I by combining appropriate volumes of the stock solutions in 100-mL volumetric flasks. Add 2 mL 1 + 1 HNO_3 and 10 mL 1 + 1 HCl and dilute to 100 mL with water. Before preparing mixed standards, analyze each stock solution separately to determine possible spectral interference or the presence of impurities. When preparing mixed standards take care that the elements are compatible and stable. Store mixed standard solutions in an FEP fluorocarbon or unused polyethylene bottle. Verify calibration standards initially using the quality control standard; monitor weekly for stability. The following are recommended combinations using the suggested analytical lines in Table 3120:I. Alternative combinations are acceptable.

1) *Mixed standard solution I:* Manganese, beryllium, cadmium, lead, selenium, and zinc.
2) *Mixed standard solution II:* Barium, copper, iron, vanadium, and cobalt.
3) *Mixed standard solution III:* Molybdenum, silica, arsenic, strontium, and lithium.
4) *Mixed standard solution IV:* Calcium, sodium, potassium, aluminum, chromium, and nickel.
5) *Mixed standard solution V:* Antimony, boron, magnesium, silver, and thallium. If addition of silver results in an initial precipitation, add 15 mL water and warm flask until solution clears. Cool and dilute to 100 mL with water. For this acid combination limit the silver concentration to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 d. Higher concentrations of silver require additional HCl.

f. Calibration blank: Dilute 2 mL 1 + 1 HNO_3 and 10 mL 1 + 1 HCl to 100 mL with water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

g. Method blank: Carry a reagent blank through entire sample preparation procedure. Prepare method blank to contain the same acid types and concentrations as the sample solutions.

h. Instrument check standard: Prepare instrument check standards by combining compatible elements at a concentration of 2 mg/L.

i. Instrument quality control sample: Obtain a certified aqueous reference standard from an outside source and prepare according to instructions provided by the supplier. Use the same acid matrix as the calibration standards.

j. Method quality control sample: Carry the instrument quality control sample (¶ 3*i*) through the entire sample preparation procedure.

k. Argon: Use technical or welder's grade. If gas appears to be a source of problems, use prepurified grade.

4. Procedure

a. Sample preparation: See Section 3030F.

b. Operating conditions: Because of differences among makes and models of satisfactory instruments, no detailed operating instructions can be provided. Follow manufacturer's instructions. Establish instrumental detection limit, precision, optimum background correction positions, linear dynamic range, and interferences for each analytical line. Verify that the instrument configuration and operating conditions satisfy the analytical requirements

and that they can be reproduced on a day-to-day basis. An atom-to-ion emission intensity ratio [Cu(I) 324.75 nm/Mn(II) 257.61 nm] can be used to reproduce optimum conditions for multielement analysis precisely. The Cu/Mn intensity ratio may be incorporated into the calibration procedure, including specifications for sensitivity and for precision.[7] Keep daily or weekly records of the Cu and Mn intensities and/or the intensities of critical element lines. Also record settings for optical alignment of the polychromator, sample uptake rate, power readings (incident, reflected), photomultiplier tube attenuation, mass flow controller settings, and system maintenance.

c. Instrument calibration: Set up instrument as directed (¶ *b*). Warm up for 30 min. For polychromators, perform an optical alignment using the profile lamp or solution. Check alignment of plasma torch and spectrometer entrance slit, particularly if maintenance of the sample introduction system was performed. Make Cu/Mn or similar intensity ratio adjustment.

Calibrate instrument according to manufacturer's recommended procedure using calibration standards and blank. Aspirate each standard or blank for a minimum of 15 s after reaching the plasma before beginning signal integration. Rinse with calibration blank or similar solution for at least 60 s between each standard to eliminate any carryover from the previous standard. Use average intensity of multiple integrations of standards or samples to reduce random error.

Before analyzing samples, analyze instrument check standard. Concentration values obtained should not deviate from the actual values by more than ±5% (or the established control limits, whichever is lower).

d. Analysis of samples: Begin each sample run with an analysis of the calibration blank, then analyze the method blank. This permits a check of the sample preparation reagents and procedures for contamination. Analyze samples, alternating them with analyses of calibration blank. Rinse for at least 60 s with dilute acid between samples and blanks. After introducing each sample or blank let system equilibrate before starting signal integration. Examine each analysis of the calibration blank to verify that no carry-over memory effect has occurred. If carry-over is observed, repeat rinsing until proper blank values are obtained. Make appropriate dilutions and acidifications of the sample to determine concentrations beyond the linear calibration range.

e. Instrumental quality control: Analyze instrument check standard once per 10 samples to determine if significant instrument drift has occurred. If agreement is not within ± 5% of the expected values (or within the established control limits, whichever is lower), terminate analysis of samples, correct problem, and recalibrate instrument. If the intensity ratio reference is used, resetting this ratio may restore calibration without the need for reanalyzing calibration standards. Analyze instrument check standard to confirm proper recalibration. Reanalyze one or more samples analyzed just before termination of the analytical run. Results should agree to within ± 5%, otherwise all samples analyzed after the last acceptable instrument check standard analysis must be reanalyzed.

Analyze instrument quality control sample within every run. Use this analysis to verify accuracy and stability of the calibration standards. If any result is not within ± 5% of the certified value, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock solution and a new calibration standard and repeat calibration.

f. Method quality control: Analyze the method quality control sample within every run. Results should agree to within ± 5% of the certified values. Greater discrepancies may reflect losses or contamination during sample preparation.

g. Test for matrix interference: When analyzing a new or unusual sample matrix verify that neither a positive nor negative nonlinear interference effect is operative. If the element is present at a concentration above 1 mg/L, use serial dilution with calibration blank. Results from the analyses of a dilution should be within ± 5% of the original result. Alternately, or if the concentration is either below 1 mg/L or not detected, use a post-digestion addition equal to 1 mg/L. Recovery of the addition should be either between 95% and 105% or within established control limits of ± 2 standard deviations around the mean. If a matrix effect causes test results to fall outside the critical limits, complete the analysis after either diluting the sample to eliminate the matrix effect while maintaining a detectable concentration of at least twice the detection limit or applying the method of standard additions.

5. Calculations and Corrections

a. Blank correction: Subtract result of an adjacent calibration blank from each sample result to make a baseline drift correction. (Concentrations printed out should include negative and positive values to compensate for positive and negative baseline drift. Make certain that the calibration blank used for blank correction has not been contaminated by carry-over.) Use the result of the method blank analysis to correct for reagent contamination. Alternatively, intersperse method blanks with appropriate samples. Reagent blank and baseline drift correction are accomplished in one subtraction.

b. Dilution correction: If the sample was diluted or concentrated in preparation, multiply results by a dilution factor (DF) calculated as follows:

$$DF = \frac{\text{Final weight or volume}}{\text{Initial weight or volume}}$$

c. Correction for spectral interference: Correct for spectral interference by using computer software supplied by the instrument manufacturer or by using the manual method based on interference correction factors. Determine interference correction factors by analyzing single-element stock solutions of appropriate concentrations under conditions matching as closely as possible those used for sample analysis. Unless analysis conditions can be reproduced accurately from day to day, or for longer periods, redetermine interference correction factors found to affect the results significantly each time samples are analyzed.[7,8] Calculate interference correction factors (K_{ij}) from apparent concentrations observed in the analysis of the high-purity stock solutions:

$$K_{ij} = \frac{\text{Apparent concentration of element } i}{\text{Actual concentration of interfering element } j}$$

where the apparent concentration of element i is the difference between the observed concentration in the stock solution and the observed concentration in the blank. Correct sample concentrations observed for element i (already corrected for baseline

drift), for spectral interferences from elements j, k, and l; for example:

$$\text{Concentration of element } i \text{ corrected for spectral interference} = \text{Observed concentration of } i - (K_{ij})\,\text{Observed concentration of interfering element } j - (K_{ik})\,\text{Observed concentration of interfering element } k - (K_{il})\,\text{Observed concentration of interfering element } l$$

Interference correction factors may be negative if background correction is used for element i. A negative K_{ij} can result where an interfering line is encountered at the background correction wavelength rather than at the peak wavelength. Determine concentrations of interfering elements j, k, and l within their respective linear ranges. Mutual interferences (i interferes with j and j interferes with i) require iterative or matrix methods for calculation.

d. Correction for nonspectral interference: If nonspectral interference correction is necessary, use the method of standard additions. It is applicable when the chemical and physical form of the element in the standard addition is the same as in the sample, *or* the ICP converts the metal in both sample and addition to the same form: the interference effect is independent of metal concentration over the concentration range of standard additions; and the analytical calibration curve is linear over the concentration range of standard additions.

Use an addition not less than 50% nor more than 100% of the element concentration in the sample so that measurement precision will not be degraded and interferences that depend on element/interferent ratios will not cause erroneous results. Apply the method to all elements in the sample set using background correction at carefully chosen off-line positions. Multielement standard addition can be used if it has been determined that added elements are not interferents.

e. Reporting data: Report analytical data in concentration units of milligrams per liter using up to three significant figures. Report results below the determined detection limit as not detected less than the stated detection limit corrected for sample dilution.

6. Precision and Bias

As a guide to the generally expected precision and bias, see the linear regression equations in Table 3120:II.[9] Additional interlaboratory information is available.[10]

TABLE 3120:II. ICP PRECISION AND BIAS DATA

Element	Concentration Range µg/L	Total Digestion* µg/L	Recoverable Digestion* µg/L
Aluminum	69–4792	$X = 0.9273C + 3.6$ $S = 0.0559X + 18.6$ $SR = 0.0507X + 3.5$	$X = 0.9380C + 22.1$ $S = 0.0873X + 31.7$ $SR = 0.0481X + 18.8$
Antimony	77–1406	$X = 0.7940C - 17.0$ $S = 0.1556X - 0.6$ $SR = 0.1081X + 3.9$	$X = 0.8908C + 0.9$ $S = 0.0982X + 8.3$ $SR = 0.0682X + 2.5$
Arsenic	69–1887	$X = 1.0437C - 12.2$ $S = 0.1239X + 2.4$ $SR = 0.0874X + 6.4$	$X = 1.0175C + 3.9$ $S = 0.1288X + 6.1$ $SR = 0.0643X + 10.3$
Barium	9–377	$X = 0.7683C + 0.47$ $S = 0.1819X + 2.78$ $SR = 0.1285X + 2.55$	$X = 0.8380C + 1.68$ $S = 0.2540X + 0.30$ $SR = 0.0826X + 3.54$
Beryllium	3–1906	$X = 0.9629C + 0.05$ $S = 0.0136X + 0.95$ $SR = 0.0203X - 0.07$	$X = 1.0177C - 0.55$ $S = 0.0359X + 0.90$ $SR = 0.0445X - 0.10$
Boron	19–5189	$X = 0.8807C + 9.0$ $S = 0.1150X + 14.1$ $SR = 0.0742X + 23.2$	$X = 0.9676C + 18.7$ $S = 0.1320X + 16.0$ $SR = 0.0743X + 21.1$
Cadmium	9–1943	$X = 0.9874C - 0.18$ $S = 0.0557X + 2.02$ $SR = 0.0300X + 0.94$	$X = 1.0137C - 0.65$ $S = 0.0585X + 1.15$ $SR = 0.0332X + 0.90$
Calcium	17–47 170	$X = 0.9182C - 2.6$ $S = 0.1228X + 10.1$ $SR = 0.0189X + 3.7$	$X = 0.9658C + 0.8$ $S = 0.0917X + 6.9$ $SR = 0.0327X + 10.1$
Chromium	13–1406	$X = 0.9544C + 3.1$ $S = 0.0499X + 4.4$ $SR = 0.0009X + 7.9$	$X = 1.0049C - 1.2$ $S = 0.0698X + 2.8$ $SR = 0.0571X + 1.0$

TABLE 3120:II. CONT.

Element	Concentration Range µg/L	Total Digestion* µg/L	Recoverable Digestion µg/L
Cobalt	17–2340	$X = 0.9209C - 4.5$ $S = 0.0436X + 3.8$ $SR = 0.0428X + 0.5$	$X = 0.9278C - 1.5$ $S = 0.0498X + 2.6$ $SR = 0.0407X + 0.4$
Copper	8–1887	$X = 0.9297C - 0.30$ $S = 0.0442X + 2.85$ $SR = 0.0128X + 2.53$	$X = 0.9647C - 3.64$ $S = 0.0497X + 2.28$ $SR = 0.0406X + 0.96$
Iron	13–9359	$X = 0.8829C + 7.0$ $S = 0.0683X + 11.5$ $SR = -0.0046X + 10.0$	$X = 0.9830C + 5.7$ $S = 0.1024X + 13.0$ $SR = 0.0790X + 11.5$
Lead	42–4717	$X = 0.9699C - 2.2$ $S = 0.0558X + 7.0$ $SR = 0.0353X + 3.6$	$X = 1.0056C + 4.1$ $S = 0.0799X + 4.6$ $SR = 0.0448X + 3.5$
Magnesium	34–13 868	$X = 0.9881C - 1.1$ $S = 0.0607X + 11.6$ $SR = 0.0298X + 0.6$	$X = 0.9879C + 2.2$ $S = 0.0564X + 13.2$ $SR = 0.0268X + 8.1$
Manganese	4–1887	$X = 0.9417C + 0.13$ $S = 0.0324X + 0.88$ $SR = 0.0153X + 0.91$	$X = 0.9725C + 0.07$ $S = 0.0557X + 0.76$ $SR = 0.0400X + 0.82$
Molybdenum	17–1830	$X = 0.9682C + 0.1$ $S = 0.0618X + 1.6$ $SR = 0.0371X + 2.2$	$X = 0.9707C - 2.3$ $S = 0.0811X + 3.8$ $SR = 0.0529X + 2.1$
Nickel	17–47 170	$X = 0.9508C + 0.4$ $S = 0.0604X + 4.4$ $SR = 0.0425X + 3.6$	$X = 0.9869C + 1.5$ $S = 0.0526X + 5.5$ $SR = 0.0393X + 2.2$
Potassium	347–14 151	$X = 0.8669C - 36.4$ $S = 0.0934X + 77.8$ $SR = -0.0099X + 144.2$	$X = 0.9355C - 183.1$ $S = 0.0481X + 177.2$ $SR = 0.0329X + 60.9$
Selenium	69–1415	$X = 0.9363C - 2.5$ $S = 0.0855X + 17.8$ $SR = 0.0284X + 9.3$	$X = 0.9737C - 1.0$ $S = 0.1523X + 7.8$ $SR = 0.0443X + 6.6$
Silicon	189–9434	$X = 0.5742C - 35.6$ $S = 0.4160X + 37.8$ $SR = 0.1987X + 8.4$	$X = 0.9737C - 60.8$ $S = 0.3288X + 46.0$ $SR = 0.2133X + 22.6$
Silver	8–189	$X = 0.4466C + 5.07$ $S = 0.5055X - 3.05$ $SR = 0.2086X - 1.74$	$X = 0.3987C + 8.25$ $S = 0.5478X - 3.93$ $SR = 0.1836X - 0.27$
Sodium	35–47 170	$X = 0.9581C + 39.6$ $S = 0.2097X + 33.0$ $SR = 0.0280X + 105.8$	$X = 1.0526C + 26.7$ $S = 0.1473X + 27.4$ $SR = 0.0884X + 50.5$
Thallium	79–1434	$X = 0.9020C - 7.3$ $S = 0.1004X + 18.3$ $SR = 0.0364X + 11.5$	$X = 0.9238C + 5.5$ $S = 0.2156X + 5.7$ $SR = -0.0106X + 48.0$
Vanadium	13–4698	$X = 0.9615C - 2.0$ $S = 0.0618X + 1.7$ $SR = 0.0220X + 0.7$	$X = 0.9551C + 0.4$ $S = 0.0927X + 1.5$ $SR = 0.0472X + 0.5$
Zinc	7–7076	$X = 0.9356C - 0.30$ $S = 0.0914X + 3.75$ $SR = -0.0130X + 10.07$	$X = 0.9500C + 1.22$ $S = 0.0597X + 6.50$ $SR = 0.0153X + 7.78$

*X = mean recovery, µg/L.
C = true value, µg/L.
S = multi-laboratory standard deviation, µg/L.
SR = single-analyst standard deviation, µg/L.

7. References

1. FAIRES, L.M., B.A. PALMER, R. ENGLEMAN, JR. & T.M. NIEMCZYK. 1984. Temperature determinations in the inductively coupled plasma using a Fourier transform spectrometer. *Spectrochim. Acta* 39B:819.
2. BARNES, R.M. 1978. Recent advances in emission spectroscopy: inductively coupled plasma discharges for spectrochemical analysis. *CRC Crit. Rev. Anal. Chem.* 7:203.
3. PARSONS, M.L., S. MAJOR & A.R. FORSTER. 1983. Trace element determination by atomic spectroscopic methods - State of the art. *Appl. Spectrosc.* 37:411.
4. LARSON, G.F., V.A. FASSEL, R. K. WINGE & R.N. KNISELEY. 1976. Ultratrace analysis by optical emission spectroscopy: The stray light problem. *Appl. Spectrosc.* 30:384.
5. GARBARINO, J.R. & H.E. TAYLOR. 1979. A Babington-type nebulizer for use in the analysis of natural water samples by inductively coupled plasma spectrometry. *Appl. Spectrosc.* 34:584.
6. AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1988. Standard specification for reagent water, D1193-77 (reapproved 1983). Annual Book of ASTM Standards. American Soc. for Testing & Materials. Philadelphia, Pa.
7. BOTTO, R.I. 1984. Quality assurance in operating a multielement ICP emission spectrometer. *Spectrochim. Acta* 39B:95.
8. BOTTO, R.I. 1982. Long-term stability of spectral interference calibrations for inductively coupled plasma atomic emission spectrometry. *Anal. Chem.* 54:1654.
9. MAXFIELD, R. & B. MINDAK. 1985. EPA Method Study 27, Method 200.7 (Trace Metals by ICP). EPA-600/S4-85/05. National Technical Information Serv., Springfield, Va.
10. GARBARINO, J.R., B.E. JONES, G. P. STEIN, W.T. BELSER & H.E. TAYLOR. 1985. Statistical evaluation of an inductively coupled plasma atomic emission spectrometric method for routine water quality testing. *Appl. Spectrosc.* 39:53.

3130 METALS BY ANODIC STRIPPING VOLTAMMETRY (PROPOSED)*

3130 A. Introduction

Anodic stripping voltammetry (ASV) is one of the most sensitive metal analysis techniques; it is as much as 10 to 100 times more sensitive than electrothermal atomic absorption for some metals. This corresponds to detection limits in the nanogram-per-liter range. The technique requires no sample extraction or preconcentration, it is nondestructive, and it may determine four to six elements simultaneously. The disadvantages of ASV are that only amalgam-forming metals can be determined, analysis time is much longer than for spectroscopic methods, and interferences and high sensitivity can present severe limitations. The analysis should be performed only by analysts skilled in its use because of the interferences and potential for trace background contamination.

* Approved by Standard Methods Committee, 1990.

3130 B. Determination of Lead and Cadmium

1. General Discussion

a. Principle: Anodic stripping voltammetry is a two-step electroanalytical technique. With pre-electrolysis, oxidized metal ions [illegible] hanging mercury drop buffer. If the pH buffer or other component of the sample matrix complexes the metal (3130B.1c), detection limits are increased.

The choice of working electrode is determined largely by the working range of concentration required. The HMDE is best suited for analysis from approximately 1 µg/L to 10 mg/L, while

discharges, or the application of herbicides. The chemical form of arsenic depends on its source (inorganic arsenic from minerals, industrial discharges, and insecticides; organic arsenic from industrial discharges, insecticides, and biological action on inorganic arsenic). The toxicity of arsenic depends on its chemical form.

2. Selection of Method

Methods are available to identify and determine arsenite, arsenate, methylarsonic acid, dimethylarsinic acid, arsenocholine, arsenobetaine, and other organic arsenic compounds. Unpolluted fresh water normally does not contain organic arsenic compounds, but may contain inorganic arsenic compounds in the form of arsenate and arsenite. The hydride generation-atomic absorption method (B), which converts arsenic compounds to their hydrides that subsequently are decomposed in an argon-hydrogen flame, is the method of choice, although the electrothermal method (direct injection of sample into the graphite tube) is simpler in the demonstrated absence of interferences. The silver diethyldithiocarbamate method (C), in which arsine is generated by sodium borohydride in acidic solution, is applicable to the determination of total inorganic arsenic when interferences are absent and the sample contains no methylarsenic compounds. Because arsenite is more toxic than arsenate, a method for identification of these two species and quantification is needed and is available in the diethyldithiocarbamate method (C). The inductively coupled plasma (ICP) method (D) is useful at higher concentrations (greater than 50 µg/L).

3500-As B. Atomic Absorption Spectrometric Method

See electrothermal atomic absorption spectrometric method, Section 3113, and hydride generation atomic absorption spectrometric method, Section 3114.

3500-As C. Silver Diethyldithiocarbamate Method

1. General Discussion

a. Principle: Arsenite, containing trivalent arsenic, is reduced selectively by aqueous sodium borohydride solution to arsine, AsH_3, in an aqueous medium of pH 6. Arsenate, methylarsonic acid, and dimethylarsenic acid are not reduced under these conditions. The generated arsine is swept by a stream of oxygen-free nitrogen from the reduction vessel through a scrubber containing glass wool or cotton impregnated with lead acetate solution into an absorber tube containing silver diethyldithiocarbamate and morpholine dissolved in chloroform. A red color develops, the intensity of which is measured at 520 nm. To determine total inorganic arsenic in the absence of methylarsenic compounds, reduce another sample portion at a pH about 1. Alternatively, determine arsenate in a sample from which arsenite has been removed by reduction at pH 6, after acidification with hydrochloric acid and addition of another portion of sodium borohydride solution. Collect the arsine formed from arsenate in fresh absorber solution.

b. Interferences: Although certain metals—chromium, cobalt, copper, mercury, molybdenum, nickel, platinum, silver, and selenium—influence the generation of arsine, their concentrations in water seldom are high enough to interfere. H_2S interferes, but the interference is removed with lead acetate. Antimony is reduced to stibine, which forms a colored complex with an absorption maximum at 510 nm and interferes with the arsenic determination. Methylarsenic compounds are reduced at pH 1 to methylarsines, which form colored complexes with the absorber solution. If methylarsenic compounds are present, measurements of total arsenic and arsenate are unreliable. The results for arsenite are not influenced by methylarsenic compounds.

c. Minimum detectable quantity: 1 µg arsenic.

2. Apparatus

a. Arsine generator, scrubber, and absorption tube: See Figure 3500-As:1. Use a 200-mL three-necked flask with a sidearm (19/22 or similar size female ground-glass joint) through which the inert gas delivery tube reaching almost to the bottom of the flask is inserted; a 24/40 female ground-glass joint to carry the scrubber; and a second side arm closed with a rubber septum, or preferably by a screw cap with a hole in its top for insertion of a TFE-faced silicon septum. Place a small magnetic stirring bar in the flask. Fit absorber tube (20 mL capacity) to the scrubber and fill with silver diethyldithiocarbamate solution. Do not use rubber or cork stoppers because they may absorb arsine. Clean glass equipment with concentrated nitric acid.

b. Fume hood: Use apparatus in a well-ventilated hood with flask secured on top of a magnetic stirrer.

c. Photometric equipment:

1) *Spectrophotometer,* for use at 520 nm.

2) *Filter photometer,* with green filter having a maximum transmittance in the 500- to 540-nm range.

3) *Cells,* for spectrophotometer or filter photometer, 1-cm, clean, dry, and each equipped with a tightly fitting cover (TFE stopper) to prevent chloroform evaporation.

3. Reagents

a. Distilled/deionized water.

b. Acetate buffer, pH 5.5: Mix 428 mL 0.2*M* sodium acetate, $NaC_2H_3O_2$, and 72 mL 0.2*M* acetic acid, CH_3COOH.

c. Sodium acetate, 0.2M: Dissolve 16.46 g anhydrous sodium acetate or 27.36 g sodium acetate trihydrate, $NaC_2H_3O_2 \cdot 3H_2O$, in water. Dilute to 1000 mL with water.

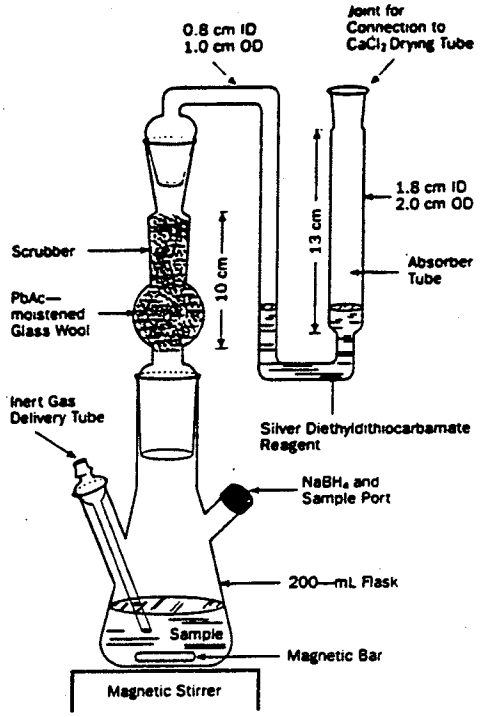

Figure 3500-As:1. Arsine generator and absorber assembly.

d. Acetic acid, 0.2*M*: Dissolve 11.5 mL glacial acetic acid in water. Dilute to 1000 mL.

e. Sodium borohydride solution, 1%: Dissolve 0.4 g sodium hydroxide, NaOH (4 pellets), in 400 mL water. Add 4.0 g sodium borohydride, $NaBH_4$ (check for absence of arsenic). Shake to dissolve and to mix. Prepare fresh every few days.

f. Hydrochloric acid, HCl, 2*M*: Dilute 165 mL conc HCl to 1000 mL with water.

g. Lead acetate solution: Dissolve 10.0 g $Pb(CH_3COO)_2 \cdot 3H_2O$ in 100 mL water.

h. Silver diethyldithiocarbamate solution: Dissolve 1.0 mL morpholine (CAUTION: *Corrosive—avoid contact with skin*) in 70 mL chloroform, $CHCl_3$. Add 0.30 g silver diethyldithiocarbamate, $AgSCSN(C_2H_5)_2$; shake in a stoppered flask until most is dissolved. Dilute to 100 mL with chloroform. Filter and store in a tightly closed brown bottle in a refrigerator.

i. Stock arsenite solution: Dissolve 0.1734 g $NaAsO_2$ in water and dilute to 1000 mL with water: 1.00 mL = 100 µg As. CAUTION: *Toxic—avoid contact with skin and do not ingest.*

j. Intermediate arsenite solution: Dilute 10.0 mL stock solution to 100 mL with water: 1.00 mL = 10.0 µg As.

k. Standard arsenite solution: Dilute 10.0 mL intermediate solution to 100 mL with water: 1.00 mL = 1.00 µg As.

l. Standard arsenate solution: Dissolve 0.416 g $Na_2HAsO_4 \cdot 7H_2O$ in water and dilute to 1000 mL. Dilute 10.0 mL to 100 mL with water: dilute 10 mL of this intermediate solution to 100 mL: 1.00 mL = 1.00 µg As.

4. Procedure

a. Arsenite:

1) Preparation of scrubber and absorber—Dip glass wool into lead acetate solution; remove excess by squeezing glass wool. Press glass wool between pieces of filter paper, then fluff it. Alternatively, if cotton is used treat it similarly but dry in a desiccator and fluff thoroughly when dry. Place a plug of loose glass wool or cotton in scrubber tube. Add 4.00 mL silver diethyldithiocarbamate solution to absorber tube (5.00 mL may be used to provide enough volume to rinse spectrophotometer cell).

2) Loading of arsine generator—Pipet not more than 70 mL sample containing not more than 20.0 µg As (arsenite) into the generator flask. Add 10 mL acetate buffer. If necessary, adjust total volume of liquid to 80 mL. Flush flask with nitrogen at the rate of 60 mL/min.

3) Arsine generation and measurement—While nitrogen is passing through the system, use a 30-mL syringe to inject through the septum 15 mL 1% sodium borohydride solution within 2 min. Stir vigorously with magnetic stirrer. Pass nitrogen through system for an additional 15 min to flush arsine into absorber solution. Pour absorber solution into a clean and dry spectrophotometric cell and measure absorbance at 520 nm against chloroform. Determine concentration from a calibration curve obtained with arsenite standards. If arsenate also is to be determined in the same sample portion save liquid in the generator flask.

4) Preparation of standard curves—Treat standard arsenite solution containing 0.0, 1.0, 2.0, 5.0, 10.0, and 20.0 µg As described in ¶s 1) through 3) above. Plot absorbance versus micrograms arsenic in the standard.

b. Arsenate: After removal of arsenite as arsine, treat sample to convert arsenate to arsine:

If the lead acetate-impregnated glass wool has become ineffective in removing hydrogen sulfide (if it has become gray to black) replace glass wool [see ¶ 4*a*1)]. Pass nitrogen through system at the rate of 60 mL/min. Cautiously add 10 mL 2.0*N* HCl. Generate arsine as directed in ¶ 4*a*3) and prepare standard curves with standard solutions of arsenate according to procedure of ¶ 4*a*4).

c. Total inorganic arsenic: Prepare scrubber and absorber as directed in ¶ 4*a*1) and load arsine generator as directed in ¶ 4*a*2) using 10 mL 2.0*N* HCl instead of acetate buffer. Generate arsine and measure as directed in ¶ 4*a*3). Prepare standard curves according to ¶ 4*a*4). Curves obtained with standard arsenite are almost identical to those obtained with arsenate standard solutions. Therefore, use either arsenite or arsenate standards.

5. Calculation

Calculate arsenite, arsenate, and total inorganic arsenic from readings and calibration curves obtained in 4*a*, *b*, and *c*, respectively, as follows:

$$\text{mg As/L} = \frac{\text{µg As (from calibration curve)}}{\text{mL sample in generator flask}}$$

6. Precision and Bias

Interlaboratory comparisons have not been made yet. The relative standard deviation of results obtained with arsenite/arsenate mixtures containing approximately 10 µg arsenic were less than 10%.

7. Bibliography

PEOPLES, S.A., J. LAKSO & T. LAIS. 1971. The simultaneous determination of methylarsonic acid and inorganic arsenic in urine. *Proc. West. Pharmacol. Soc.* 14:178.

AGGETT, J. & A.C. ASPELL. 1976. Determination of arsenic (III) and total arsenic by the silver diethyldithiocarbamate method. *Analyst* 101:912.

HOWARD, A.G. & M.H. ARBAB-ZAVAR. 1980. Sequential spectrophotometric determination of inorganic arsenic (III) and arsenic (V) species. *Analyst* 105:338.

PANDE, S.P. 1980. Morpholine as a substitute for pyridine in determination of arsenic in water. *J. Inst. Chem. (India)* 52:256.

IRGOLIC, K.J. 1986. Arsenic in the environment. *In* A. V. Xavier, ed. Frontiers in Bioinorganic Chemistry. VCH Publishers, Weinheim, Germany.

IRGOLIC, K.J. 1987. Analytical procedures for the determination of organic compounds of metals and metalloids in environmental samples. *Sci. Total Environ.* 64:61.

3500-As D. Inductively Coupled Plasma Method

See Section 3120.

3500-Ba BARIUM*

3500-Ba A. Introduction

1. Occurrence and Significance

Barium stimulates the heart muscle. However, a barium dose of 550 to 600 mg is considered fatal to human beings. Afflictions arising from its consumption, inhalation, or absorption involve the heart, blood vessels, and nerves.

Despite a relative abundance in nature (16th in order of rank), barium occurs only in trace amounts in water. The barium concentration of U.S. drinking waters ranges between 0.7 and 900 µg/L, with a mean of 49 µg/L. Higher concentrations in drinking water often signal undesirable industrial waste pollution.

2. Selection of Method

Perform analyses by the atomic absorption spectrometric method or the inductively coupled plasma method.

*Approved by Standard Methods Committee, 1990.

3500-Ba B. Atomic Absorption Spectrometric Method

See flame atomic absorption spectrometric method, Section 3111D, and electrothermal atomic absorption spectrometric method, Section 3113.

3500-Ba C. Inductively Coupled Plasma Method

See Section 3120.

APPENDIX 2

BIBLIOGRAPHY OF ARSENIC CHEMISTRY AND ARSENIC SPECIATION ANALYTICAL METHODS

APPENDIX 2

BIBLIOGRAPHY

Aurillo, A.C., R.P. Mason, and H.F. Hemond, (1994), "Speciation and Fate of Arsenic in Three Lakes of the Aberjona Watershed," *Environmental Science and Technology,* Vol 28, pp. 577-585.

Blais, J.S., G.M. Momplaisir, and W.D. Marshall, (1990), "Determination of Arsenobetaine, Arsenochoine, and Tetramethylarsonium Cations by Liquid Chromatography-Thermochemical Hydride Generation-Atomic Absorption Spectrometry," *Analytical Chemistry*, Vol 62, pp. 1161-1166.

Bushee, D.S., I.S. Krull, P.R. Demko, and S.B. Smith, (1984), "Trace Analysis and Speciation for Arsenic Anions by HPLC-Hydride Generation-Inductively Coupled Plasma Emission Spectroscopy," *Journal of Liquid Chromatography*, Vol 7, No. 5, pp. 861-876.

Ferguson, J.F. and J. Gavis, (1972), "A Review of the Arsenic Cycle in Natural Waters," *Water Research*, Pergaman Press, Vol 6.

Gjerde, D.T., D.R. Wiederin, F.G. Smith, and B.M. Mattson, (in preparation). "Metal Speciation Using Microbore Columns with Direct Injection Nebulization by Inductively Coupled Plasma: Atomic Emission Spectroscopy."

Hansen, S.H., E.H. Larsen, G. Pritzl, and C. Cornett, (June 1992), "Separation of Seven Arsenic Compounds by High-Performance Liquid Chromatography with On-Line Detection by Hydrogen-Argon Flame Atomic Absorption Spectrometry and Inductively Coupled Plasma Mass Spectrometry," *Journal of Analytical Atomic Spectrometry*, Vol 7.

Iadevaia, R., N. Aharonson, and E. A. Woolson, (1980), "Extraction and Cleanup of Soil Arsenical Residues for Analysis by High Pressure Liquid Chromatographic - Graphite Furnace Atomic Adsorption," US Department of Agriculture, *Analytical Chemistry*, Vol 63, No. 4.

Illinois Administrative Code, Title 35, Environmental Protection, Subtitle C, *Water Pollution*, Chapter 1 - Pollution Control Board, (Adopted March 7, 1972, as amended through December 18, 1990).

Indiana Administrative Code, Title 327, Water Pollution Control Board, Articles 1 and 2, *Water Quality Standards*, (Adopted January 10, 1953 and last amended March 3, 1990).

Irgolic, K.J., R.A. Stockton, and D. Chakraborti, (1981), "Determination of Arsenic and Arsenic Compounds in Water Supplies," Arsenic Symposium, Gaithersburg, Maryland.

Low, G.K, G.E. Batley, and S.J. Buchanan, (1986), "Application of Column Switching in High-Performance Liquid Chromatography to Arsenic Speciation Analysis with Inductively Coupled Argon Plasma Spectrometric Detection," *Journal of Chromatography*, Vol 368, pp. 423-426.

McCarthy, J.P., J.A. Caruso, and F.L. Fricke, (September 1983), "Speciation of Arsenic and Selenium via Anion-Exchange HPLC with Sequential Plasma Emission Detection," *Journal of Chromatographic Science*, Vol 21.

Michigan Administrative Code, Department of Natural Resources, Water Resources Commission General Rules, Part 4 - *Water Quality Standards*, (Adopted effective December 13, 1973 and last amended November 29, 1986).

Minnesota Rules, Chapter 7050 - Minnesota Pollution Control Agency, Water Quality Division, *Waters of the State*, (Amended through November 5, 1990).

Missouri Code of State Regulations, Title 10, Department of Natural Resources, Division 20, Clean Water Commission, Chapter 7 - *Water Quality*, (Adopted effective December 11, 1977 and last amended March 14, 1991).

New York Codes, Rules and Regulations, Title 6, Environmental Conservation, Chapter X - Division of Water Resources, Parts 700-704, (Adopted effective April 28, 1972 and last amended January 7, 1994).

Ohio Administrative Code, Title 3745, Environmental Protection Agency, Chapter 1 - *Water Quality Standards*, (Adopted January 31, 1977 and last amended September 30, 1993).

Pennsylvania Code, Title 25, Environmental Resources, Chapter 93 - *Water Quality Standards*, (Adopted September 3, 1971 and last amended February 12, 1994).

Seydel, I.S., (1972), "Distribution and Circulation of Arsenic through Water, Organisms, and Sediments of Lake Michigan," *Archives of Hydrobiology*, Vol 71, No. 1, pp. 17-30.

Spall, W.D., J.G. Lynn, J.L. Anderson, J.G. Valdez, and L.R. Gurley, (1986), "High-Performance Liquid Chromatographic Separation of Biologically Important Arsenic Species Utilizing On-Line Inductively Coupled Argon Plasma Atomic Emission Spectrometric Detection," *Analytical Chemistry*, Vol 58, No. 7, pp. 1340-1344.

Standard Methods for the Analysis of Water and Waste, 18th edition, 1992.

USDHEW, Registry of Toxic Effects of Chemical Substances, Section 2, 1978.

USEPA, Office of Research and Development (February 1986), *Arsenic (III) Oxidation and Removal from Drinking Water*, (EPA/600/2-86/021).

USEPA, *Ambient Water Quality Criteria for Arsenic*, (October 1980).

USEPA, "Proposed Water Quality Guidance for the Great Lakes System," (April 16, 1993) Vol 58, *Federal Register*, EPA 20802-21047.

USEPA, *Quality Criteria for Water 1986*, (May 1986 and first update September 2, 1986).

USEPA, *Regulations and Test Procedures for Analysis of Pollutants*, (40 CFR 136).

USEPA, *Toxicological Profile for Arsenic*, Agency for Toxic Substances and Disease Registry, U.S. Public Health Service, November 1987.

USEPA, Office of Research and Development (June 1991), *Project Summary Arsenic (III) and Arsenic (V) Removal from Drinking Water in San Ysidro, New Mexico*, (EPA 600/S2-91/011).

Violante, F., F. Petrucci, F. La Torre, and S. Caroli, (September 1992), "On-Line Speciation and Quantification of Arsenic Using an HPLC-UV-HG-ICP-AES System," *Spectroscopy*.

Wagemann, R., (1978), "Some Theoretical Aspects of Stability and Solubility of Inorganic Arsenic in the Freshwater Environment," *Water Research*, Vol 12, pp. 139-145.

Wisconsin Administrative Code, Wisconsin Water Quality Standards, Chapters NR 100 through 108, (Adopted April 1, 1971 and last amended June 1, 1993).

Woolson, E.A. and N. Aharonson, (1980), "Separation and Detection of Arsenical Pesticide Residues and Some of Their Metabolites by High Pressure Liquid Chromatography - Graphite Furnace Atomic Adsorption Spectrometry," US Department of Agriculture, *Analytical Chemistry*, Vol 63, No. 3.

APPENDIX 3

EPL BIO-ANALYTICAL SERVICES, INC.

ANALYTICAL METHOD FOR ARSENIC SPECIATION

Bio · Analytical Services, Inc.
Quality, Integrity & Commitment℠

RESEARCH CAMPUS SITES

Illinois

P.O. Box 109
395 N. Memorial Parkway
Harristown, IL 62537-0109

Phone: 217-963-2143
Fax: 217-963-2283

Florida

P.O. Box 771084
Winter Garden, FL 34777-1084

6636 Cook Road
Clermont, FL 34711

Phone: 904-394-4535
Fax: 904-394-4433

QA/QC Plan for:
EPL-BAS Project Number 251M01
Analysis of Water for Total Arsenic, Arsenite and Arsenate
Client: Amoco Oil Company
Client Contact: Natalie Grimmer

Laboratory QC Matrix Spikes

EPL-BAS will analyze quality control (QC) spikes as part of this project. The preparation of QC spikes is described in section III.A.3. of the analytical method. A single QC spike will be analyzed with each batch of water samples received at EPL-BAS. The spike will contain both arsenite and arsenate at a target concentration of 20-50 µg/L As for each compound. QC spike recoveries will be calculated as follows.

$$\frac{\text{Spike Concentration } (\mu g/L) - \text{Unspiked Concentration } (\mu g/L)}{\text{Spike Level } (\mu g/L)} \times 100$$

QC spike recoveries shall be in the range of 70-125%. Recoveries outside this range will necessitate preparation of a new QC spike and reanalysis of all water samples in that batch.

Quality Assurance Data Review

The Laboratory Supervisor will review the raw data for completeness of documentation and to confirm that QC results are within acceptance limits. The Laboratory Supervisor will also review the final analytical report to assure that the report is an accurate reflection of the raw data.

Determination of Total Soluble Arsenic and Arsenic Species in Water using Graphite Furnace Atomic Absorption Techniques

Method Summary:

Water samples are filtered and diluted as necessary for analysis. Arsenic speciation analysis is performed using anion exchange HPLC with graphite furnace atomic absorption (GFAA) detection. Filtered samples are also analyzed by GFAA with Zeeman background correction for total soluble arsenic.

I. Standards, Reagents, and Solutions

A. Standards

Arsenic Reference Solution, Certified 1000 ppm, Fisher
Sodium Arsenite, Fisher Scientific, 99%+
Sodium Arsenate, Fisher Scientific, 98%+

B. Reagents

Ammonium Carbonate, Mallinckrodt
Nickel Nitrate Hexahydrate, Aldrich
Water, ASTM Type I

C. Solution Preparation

1. HPLC Eluent (0.2M ammonium carbonate)

Weigh 44 g ammonium carbonate into a 2 L volumetric flask and dilute to volume with Type I water. Store ambient.

2. Calibration Standard Solutions (for total As analysis)

Prepare standards in Type I water by appropriate dilution of the 1000 ppm As reference solution noted above. A concentration range of approximately 5 to 100 µg/L As should be prepared. Store standards frozen.

3. Reference Standard Solutions (for speciation analysis)

Dissolve appropriate amounts of sodium arsenite and sodium arsenate in Type I water. Store stock standards frozen. Prepare working reference standards by appropriate dilution of the stock solutions in Type I water. Store working standards frozen.

4. GFAA Matrix Modifier (0.4% Ni)

Weigh 2 g nickel nitrate hexahydrate into a 100 mL volumetric flask and dilute to volume with Type I water. Store ambient.

II. Equipment

Balances, Mettler, Sartorius, and American Scientific
Class A Glassware, acid-washed*
Atomic Absorption Spectrophotometer, Perkin-Elmer Model 460 equipped with an AS-1 Autosampler and HGA-2100 Graphite Furnace.
Atomic Absorption Spectrophotometer, Perkin-Elmer Zeeman 30/30 equipped with an AS-60 autosampler and HGA-600 Graphite Furnace.
Filters, 0.45 μm Acrodiscs, Gelman
HPLC Pump, Perkin-Elmer Model 410
Arsenic Electrodeless Discharge Lamp, Perkin-Elmer
Switching Valve, Valco Instruments
LC Autosampler, Micromiretics

*All glassware and sample storage containers are soaked overnight and thoroughly washed with detergent and tap water, rinsed with water, and soaked for four hours in a mixture of dilute nitric and hydrochloric acid (1:2:9), followed by rinsing with ASTM Type I water and oven drying.

III. Methodology

A. Sample Preparation

1. Store water samples frozen upon receipt.
2. Filter a suitable aliquot of thawed water sample through a 0.45 μm filter. Use the first 10-20 mL to rinse the filter and collect the remainder of the sample for analysis.
3. Prepare a QC spike at ca 20-50 μg/L As for each; arsenite and arsenate, by addition of aqueous reference standard solutions to a water sample of known volume. A single QC spike is to be prepared and analyzed with each batch of water samples received.

B. Total Arsenic Analysis

Total soluble arsenic analysis is performed by GFAA with Zeeman background correction. Recommended analysis conditions are as follows.

Spectrometer:	Wavelength:	193.7 nm
	Slit:	0.7 nm
	Lamp:	Arsenic electrodeless discharge lamp operated at ca 8 Watts.
Furnace Program:	Dry Time:	30 seconds
	Dry Temp:	120°C
	Char Time:	30 seconds
	Char Temp:	1300°C
	Atomization Time:	5 seconds
	Atomization Temp:	2350°C
Autosampler:	Sample Injection Volume:	20 µL
	Matrix Modifier (0.4% Ni):	5 µL

Calibration is performed by analysis of standards containing from ca 5 to 100 µg/L elemental As.

C. Speciation Analysis

Speciation analysis is performed by anion exchange HPLC with GFAA detection. Recommended analysis conditions are as follows.

GFAA

Slit:	0.7 nm
Wavelength:	193.7 nm
Lamp:	Arsenic electrodeless discharge lamp operated at ca 8 Watts
Dry Temp:	130°C
Dry Time:	ca 20 seconds
Char Temp:	800°C
Char Time:	ca 8 seconds
Atomization Temp:	2300°C
Atomization Time:	5 seconds
GFAA Autosampler Injection Volume:	10 µL

HPLC

Solvent A — HPLC Water
Solvent B — 0.2M $(NH_4)_2CO_3$

Column: 2 Brownlee Polypore AN (4.6 x 60 mm) anion exchange guard columns.

Solvent Program:

Time	% Solvent	Flow (mL/minute)	Curve
Initial	100 A	0.5	—
20 minutes	100 B	0.5	1
30 minutes	100 A	2.0	1
44 minutes	100 A	0.5	—

Alternative HPLC Technique:

Column: 1 Alltech Universal Anion Exchange HPLC column (4.6 x 150 mm).

Solvent Program:

Time	% Solvent	Flow (mL/minute)	Curve
Initial	100 A	0.5	—
30 minutes	65 A/35 B	0.5	1
40 minutes	100 B	0.5	1
50 minutes	100 A	2.0	1
52 minutes	100 A	0.5	—

Reference standards are analyzed to ascertain retention times for the inorganic arsenicals. Quantitation of each arsenical detected will be by cumulative peak height percent (see calculations).

IV. Calculations

A. Total Soluble As (μg/L) =

Analytical Result (μg/L) x Dilution Factor

B. Speciated As (μg/L As) =

Cumulative Peak Height Percent for Compound ___ x Total As (μg/L)

Where Peak Height Percent =

$$\frac{\text{Cumulative Peak Height for Compound}}{\text{Sum of Cumulative Peak Heights for all Compounds}}$$

APPENDIX 4

ARSENIC SPECIATION ANALYTICAL REPORTS

AMOCO RESEARCH AND DEVELOPMENT LABORATORY

Naperville, Illinois

- Data Validation
- Summary Metals Tables

SUMMARY OF DATA VALIDATION FOR NPDES PERMIT APPLICATION
ARSENIC TOTAL ANALYSES FOR OUTFALL 001 EFFLUENT (a)

	LAB (Analytical) VALIDATION (b)	FIELD VALIDATION (b)	COMPLETE VALIDATION (c)
SAMPLE 4 May 94	A	A	A
SAMPLE 10 May 94	A	A	A
SAMPLE 17 May 94	J	A	J
SAMPLE 26 May 94	A	J	J
SAMPLE 1 Jun 94	J	A	J
SAMPLE 7 Jun 94	A	A	A

Notes:
(a) Analysis by Amoco Research and Development Laboratory, Naperville, Laboratory
(b) A = Totally Acceptable
J = Estimated Value because of QA/QC question
(c) Complete Validation is a combination of lab and field validations.

Table 1

Whiting ETL Wastewater (Outfall 001) - 1/14/94
(Results given in micrograms/liter or ppb)

	12938-75-Total	12938-75-Dissolved
Part B Metals		
Aluminum	49	17
Barium	90	88
Boron	260	260
Cobalt	ND < 3	ND < 3
Iron	130	20
Magnesium	18000	20000
Molybdenum	20	16
Manganese	107	94
Tin	ND < 7	ND < 7
Titanium	ND < 7	ND < 7
Part C Metals		
Antimony	ND < 20	20
Arsenic	14	14
Beryllium	2	2
Cadmium	ND < 2	ND < 2
Chromium	ND < 10	ND < 10
Copper	16	6
Lead	11	ND < 1
Mercury	ND < 0.5	ND < 0.5
Nickel	ND < 7	ND < 7
Selenium	39	38
Silver	ND < 5	ND < 5
Thallium	ND < 2	ND < 2
Zinc	31	23

Re-analysis for total metals: Magnesium = 17600; Manganese = 80; Iron = 80; Copper = 15; Zinc = 25.

Gary R. Chipman
August 17, 1994

Table 2

Whiting Quality Control Samples - 1/14/94
(Results given in micrograms/liter or ppb)

	Field Blank	Trip Blank	Equip. Blank
Part B Metals			
Aluminum	ND < 4	ND < 4	ND < 4
Barium	ND < 1	ND < 1	ND < 1
Boron	ND < 20	ND < 20	ND < 20
Cobalt	ND < 3	ND < 3	ND < 3
Iron	ND < 10	ND < 10	40
Magnesium	ND < 1	ND < 1	22
Molybdenum	ND < 5	ND < 5	ND < 5
Manganese	ND < 1	ND < 1	2
Tin	ND < 7	ND < 7	ND < 7
Titanium	ND < 7	ND < 7	ND < 7
Part C Metals			
Antimony	ND < 20	ND < 20	ND < 20
Arsenic	ND < 1	ND < 1	ND < 1
Beryllium	ND < 1	ND < 1	ND < 1
Cadmium	ND < 2	ND < 2	ND < 2
Chromium	ND < 10	ND < 10	ND < 10
Copper	ND < 3	ND < 3	ND < 3
Lead	ND < 1	ND < 1	48
Mercury	ND < 0.5	ND < 0.5	ND < 0.5
Nickel	ND < 7	ND < 7	9
Selenium	ND < 3	ND < 3	ND < 3
Silver	ND < 5	ND < 5	ND < 5
Thallium	ND < 2	ND < 2	ND < 2
Zinc	ND < 1	ND < 1	5

Analytical Research & Services Division source record numbers: CARN 94-001269 and 94-001536.

Gary R. Chipman
August 17, 1994

Table 3

Whiting ETL Wastewater (Outfall 001) - 2/11/94
(Results given in micrograms/liter or ppb)

	12938-80-Total	12938-80-Dissolved
Part B Metals		
Aluminum	77	23
Barium	68	69
Boron	210	200
Cobalt	ND < 3	ND < 3
Iron	180	10
Magnesium	17000	19100
Molybdenum	20	20
Manganese	34	32
Tin	ND < 7	ND < 7
Titanium	ND < 7	ND < 7
Part C Metals		
Antimony	ND < 20	ND < 20
Arsenic	20	21
Beryllium	ND < 1	ND < 1
Cadmium	ND < 2	ND < 2
Chromium	14	ND < 10
Copper	16	4
Lead	10	ND < 1
Mercury	ND < 0.5	ND < 0.5
Nickel	ND < 7	ND < 7
Selenium	36	30
Silver	ND < 5	ND < 5
Thallium	ND < 2	ND < 2
Zinc	74	27

Re-analysis for total metals: Magnesium = 14600; Aluminum = 62; Iron = 120; Copper = 16; Zinc = 33.

Gary R. Chipman
August 17, 1994

Table 4

Whiting Quality Control Samples - 2/11/94

	Field Blank	Trip Blank
Part B Metals		
Aluminum	15	13
Barium	ND < 1	ND < 1
Boron	ND < 20	ND < 20
Cobalt	ND < 3	ND < 3
Iron	ND < 10	ND < 10
Magnesium	39	36
Molybdenum	ND < 5	ND < 5
Manganese	ND < 1	ND < 1
Tin	ND < 7	ND < 7
Titanium	ND < 7	ND < 7
Part C Metals		
Antimony	ND < 20	ND < 20
Arsenic	1	1
Beryllium	ND < 1	ND < 1
Cadmium	ND < 2	ND < 2
Chromium	ND < 10	ND < 10
Copper	ND < 3	ND < 3
Lead	ND < 1	ND < 1
Mercury	ND < 0.5	ND < 0.5
Nickel	ND < 7	ND < 7
Selenium	3	ND < 3
Silver	ND < 5	ND < 5
Thallium	ND < 2	ND < 2
Zinc	ND < 1	ND < 1

Analytical Research & Services Division source record numbers: CARN 94-002714 and 94-003103.

Gary R. Chipman
August 17, 1994

Table 5

Whiting ETL Wastewater (Outfall 001) - 3/2/94
(Results given in micrograms/liter or ppb)

	12938-83-Tot	12938-83-Dis	Trip Blank
Part B Metals			
Aluminum	51	26	46
Barium	76	79	ND < 1
Boron	230	240	ND < 20
Cobalt	ND < 3	ND < 3	ND < 3
Iron	100	20	10
Magnesium	18500	19900	50
Molybdenum	19	21	ND < 5
Manganese	31	28	ND < 1
Tin	ND < 7	ND < 7	ND < 7
Titanium	ND < 7	ND < 7	ND < 7
Part C Metals			
Antimony	ND < 20	ND < 20	ND < 20
Arsenic	12	11	ND < 1
Beryllium	ND < 1	ND < 1	ND < 1
Cadmium	ND < 2	ND < 2	ND < 2
Chromium	ND < 10	ND < 10	ND < 10
Copper	18	4	ND < 3
Lead	7	ND < 1	ND < 1
Mercury	ND < 0.5	ND < 0.5	ND < 0.5
Nickel	ND < 7	ND < 7	ND < 7
Selenium	30	25	ND < 3
Silver	ND < 5	ND < 5	ND < 5
Thallium	ND < 2	ND < 2	ND < 2
Zinc	24	17	ND < 1

Analytical Research & Services Division source record numbers: CARN 94-003752 and 94-003946.

Gary R. Chipman
August 17, 1994

Table 6

Whiting ETL Wastewater (Outfall 001) - 3/9/94
(Results given in micrograms/liter or ppb)

	ETL-Total	ETL-Dissolved	Trip Blank
Part B Metals			
Aluminum	62	32	ND < 4
Barium	58	58	ND < 1
Boron	240	240	ND < 20
Cobalt	ND < 3	ND < 3	ND < 3
Iron	100	20	ND < 10
Magnesium	18300	20200	13
Molybdenum	81	73	ND < 5
Manganese	26	24	ND < 1
Tin	ND < 7	ND < 7	ND < 7
Titanium	ND < 7	ND < 7	ND < 7
Part C Metals			
Antimony	ND < 20	ND < 20	ND < 20
Arsenic	16	17	ND < 1
Beryllium	ND < 1	ND < 1	ND < 1
Cadmium	ND < 2	ND < 2	ND < 2
Chromium	10	ND < 10	ND < 10
Copper	18	6	ND < 3
Lead	11	ND < 1	ND < 1
Mercury	ND < 0.5	ND < 0.5	ND < 0.5
Nickel	ND < 7	ND < 7	ND < 7
Selenium	33	31	ND < 3
Silver	ND < 5	ND < 5	ND < 5
Thallium	ND < 2	ND < 2	ND < 2
Zinc	26	18	ND < 1

Analytical Research & Services Division source record numbers: CARN 94-004270 and 94-004582.

Gary R. Chipman
August 17, 1994

Table 7

Whiting ETL Wastewater (Outfall 001) - 4/14/94
(Results given in micrograms/liter or ppb)

	Blank	ETL-Total	ETL-Dissolved	Trip
Arsenic		18	11	2
Cadmium		ND < 2	ND < 2	ND < 2
Copper		10	5	ND < 3
Lead		8	1	ND < 1
Nickel		ND < 7	ND < 7	ND < 7
Zinc		20	16	ND < 1

Analytical Research & Services Division source record numbers: CARN 94-006855 and 94-006888.

Gary R. Chipman
August 17, 1994

Table 8

Whiting ETL Wastewater (Outfall 001) - 4/26/94
(Results given in micrograms/liter or ppb)

	Blank	ETL-Total	ETL-Dissolved	Trip
Arsenic		13	16	ND < 1
Cadmium		ND < 2	ND < 2	ND < 2
Copper		8	ND < 3	ND < 3
Lead		4	ND < 1	ND < 1
Nickel		ND < 7	ND < 7	ND < 7
Zinc		15	16	ND < 1

Analytical Research & Services Division source record numbers: CARN 94-006781 and 94-006838.

Gary R. Chipman
August 17, 1994

Table 9

Whiting ETL Wastewater (Outfall 001) Collected during May and June, 1994, for Arsenic Analysis (Results given in micrograms/liter of ppb)

Collection Date	Sample No.	Arsenic ug/L
5/4/94	ETL-001	NA
	2-N-0	16
	2-N-1	16
	2-N-2	420
	2-N-3	ND <1
5/10/94	ETL-001	18
	Trip Blank	NA
5/17/94	ETL-001	17
5/26/94	5-N-0	16
	5-N-1	15
	5-N-2	250
	5-N-3	4
6/1/94	6-N-0	21
6/7/94	7-N-0	13
	7-N-1	12
	7-N-2	433
	7-N-3	ND <1

Analytical Research & Services Division source record numbers: CARN 94-006232, 94-006506, 94-006551, 94-006654, 94-006963, 94-007447, 94-007608, 94-007978, 94-007979, 94-008146 and 94-008318.

Gary R. Chipman
August 17, 1994

94230NAP0055

EPL BIO-ANALYTICAL, INC.

Harristown, Illinois

- Project Report
- Sample Chromatograms

PROJECT TITLE

Analysis of Wastewater for Total Soluble Arsenic and Soluble Arsenic Species

CLIENT

Amoco Oil Company - Whiting Refinery
Environmental Control
2815 Indianapolis Blvd. Mail Code 242
Whiting, IN 46394

AUTHOR

Fred A. Claussen, B.S.

PERFORMING LABORATORY

EPL Bio-Analytical Services, Inc. (EPL-BAS)
P.O. Box 109
Harristown, IL 62537
(217)963-2143

LABORATORY PROJECT IDENTIFICATION

251M01

List of Tables

List of Appendices

I. Abstract

Wastewater samples taken over a seven week period at the Whiting, Indiana Amoco Oil Refinery were analyzed for total soluble arsenic and arsenic species using two graphite furnace atomic absorption (GFAA) techniques. Total soluble arsenic was determined on filtered water samples by GFAA with Zeeman Effect background correction. Total soluble arsenic levels ranged from < 5 μg/L to 620 μg/L As. Arsenic speciation analysis was performed by first separating the arsenicals on an anion-exchange HPLC column and analyzing the HPLC effluent by GFAA. Only inorganic arsenic was detected in the wastewater samples. Arsenate was the predominate form found in the samples. Three samples contained detectable levels of arsenite. Quality control (QC) samples were analyzed as part of this project. QC samples were prepared by spiking aliquots of a randomly selected filtered wastewater sample at approximately 50 μg/L As in inorganic form; one QC each for arsenate and arsenite. The QC samples were prepared and analyzed for total soluble arsenic and arsenic species as described above for the unspiked waste samples. QC recoveries ranged from 91 to 99 percent for samples spiked at 50 μg/L As as arsenite and from 83 to 91 percent for those spiked with an equivalent amount of arsenate.

II. Materials/Methods

A description of the laboratory procedures used in the project follows. The analytical method appears in Appendix B. All wastewater samples were stored frozen upon receipt at EPL-BAS.

A. Total Soluble Arsenic Determination

Waste samples were first filtered through a 0.45 μm Acrodisc®. Filtrates were stored frozen until needed for analysis. No additional sample preparation was required for total soluble arsenic determination. QC samples were prepared by pipeting 50 μL of a 100 μg/mL arsenic solution containing either arsenate or arsenite into a 100 mL volumetric flask and diluting to 100 mL with a randomly chosen waste sample. Two QC samples, 1 each for arsenate and arsenite, were analyzed with each batch of samples. Samples were analyzed using a Perkin-Elmer Zeeman 30/30 Atomic Absorption Spectrophotometer equipped with an AS-60 Autosampler and HGA-600 Graphite Furnace. The instrument was calibrated prior to sample analysis by injection of aqueous standard solutions containing from 20 to 100 μg/L As. The calibration standards were prepared by dilution of a certified reference solution containing 1000 mg/L As. The instrument software produces a calibration curve by linear regression analysis. Sample concentrations are also calculated by the instrument software based on the calibration curve. The instrumental detection limit was estimated at 5 μg/L As.

B. Speciation Analysis

Speciation analysis was performed using an HPLC/GFAA technique. If required, samples were concentrated under nitrogen to bring the arsenic concentration to a detectable level. The degree of concentration was based on the total soluble arsenic level. Sample solutions were injected (100 μL) into an HPLC system containing two low-capacity anion-exchange columns. Arsenicals are separated based on anionic charge. Highly charged arsenicals are retained more strongly than those of lower charge. The compounds are eluted from the column by introduction of carbonate ion into the HPLC mobile phase. The carbonate concentration is slowly increased until all arsenicals have eluted. The HPLC effluent is diverted to a continuous flow cup which is sampled by a GFAA autosampler. The GFAA autosampler deposits a 10 μL subsample of the HPLC effluent into the graphite furnace. The furnace dries, ashes, and then atomizes the subsamples. Arsenic in the subsample is detected by the spectrometer which plots an absorption signal. This cycle repeats approximately once every 45 seconds with the resulting chromatograms appearing as a bar graph. Standard solutions containing arsenate and arsenite at approximately 500 μg/L As were analyzed along with the samples for retention time verification and to ascertain detector response. Typically, the relative amount of each arsenical detected is calculated directly using the peak height for each compound. However, if detector responses for standards containing different compounds at the same concentration results in a difference of >10 percent, a response factor based on the standard concentration is used to calculate the relative amounts of each compound. Some typical chromatograms appear in Appendix B. The instrument detection limit was estimated at 100 μg/L As for each compound; arsenite and arsenate. The method limit of detection based on a 20X concentration factor was 5 μg/L.

III. Results

Quality control recoveries were good in general. The results for QC sample analyses appear in Table I. Little or no oxidation/reduction between arsenate and arsenite occurred during spike sample processing in the laboratory. The same assumption can probably be made for unspiked samples as well. Recoveries for arsenite spikes ranged from 91 to 99 percent with an overall mean recovery of 95 percent and a standard deviation of 4.0 percent. The range of recoveries for arsenate spikes was 83 to 91 percent with an overall mean recovery of 87 percent and a standard deviation of 4.0 percent.

Wastewater analysis results appear in Table II. Unspiked wastewater samples displayed a wide range of arsenic concentrations. Detectable arsenic concentrations ranged from 11 to 620 μg/L. HPLC/GFAA analysis indicated that arsenate was the predominate form with three samples having approximately equal amounts of arsenate and arsenite (see Table II.)

IV. Tables